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MEMORANDUM FOR PR (Contractor/In-House Publication)

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30 Oct 2000

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Drake, Greg; Tollison, Kerri (ERC); Hawkins, Tom; Brand, Adam; McKay, Milton; Ismail, Ismail
(ERC) "The Synthesis and Characterization of New Energetic Salts" (Extended Abstract for HEDM
Proceedings)

**2000 USAF High Energy Density Matter Contractors' Conference
(Park City, UT, 24-26 Oct 2000) - Extended Abstract for Proceedings**

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PHILIP A. KESSEL Date
Technical Advisor
Propulsion Science and Advanced Concepts Division

The Synthesis and Characterization of New Energetic Salts

Greg Drake; Kerri Tollison*; Tom Hawkins; Adam Brand; Milton McKay; Ismail Ismail*

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Presently, hydrazine is the state of the art in many attitude control devices on many currently used satellite systems. The physical properties of hydrazine, namely its density and high vapor pressure, have led several research groups to search for new superior materials. In the late 1980's and through most of the 1990's significant amounts of work were placed on two low melting salt, hydroxylammonium nitrate (HAN), and hydroxylammonium dinitramide (HADN). These two salts have from 60-70% density increase over that of hydrazine and when formulated with various fuels, make for energetic propellant materials. Unfortunately, hydroxylammonium nitrate and dinitramide salts have many safety, compatibility, storage, and ignition problems. At the Air Force Research Laboratory, we have been pursuing the synthesis and characterization of new energetic salts, as new monopropellant ingredients. Herein, we will discuss our synthetic work with a new large array of energetic salts based on high nitrogen, 1, 2, 4-triazoles, and on the very energetic 1, 2-bis(oxyamino)ethane. This discussion will include the synthesis, characterization, initial small scale safety testing (impact and friction), and some initial thermal stability studies of all these salts.

It was realized that there are several, easily synthesized, nitrogen heterocycles that could be paired with anions including the nitrate, perchlorate, and dinitramide anions to form highly energetic salts. The four heterocycle systems are 1,2,4-triazole; 4-amino-1,2,4-triazole; 3,4,5-triamino-1,2,4-triazole; and 1,2,3-triazole (Figure 1). All of these heterocycles are either commercially available or are easily synthesized in high yield from inexpensive starting materials, and all have high heats of formation. Except for one Russian report on a complex between 4-amino-1,2,4-triazole and trinitromethane¹, salts of these heterocycles have not been addressed by researchers in the field of energetic materials. The heats of formation were calculated using simple bond additivities, from well-known similar compounds. Protonating these heterocycles with strong acids of energetic anions such as HNO_3 , HClO_4 , and $\text{HN}(\text{NO}_2)_2$ would form many new salts that would meet the objectives of high heat of formation and high density for ingredients of high performance propellants.

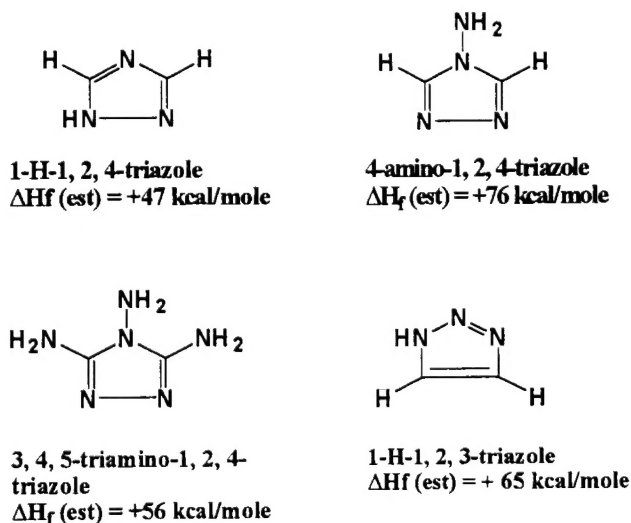
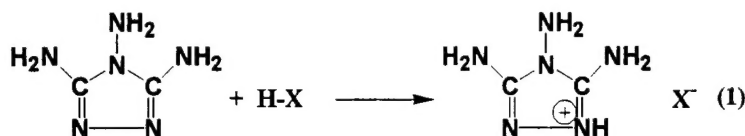


Figure 1: The heterocycle systems under study.

The synthesis of 3, 4, 5-triamino-1, 2, 4-triazole, guanazine, is a facile process and involves the reaction of hydrazine and dimethylcyanamide at elevated temperatures.² Energetic salts of guanazine were made through the simple reaction of one equivalent of the heterocycle with one equivalent of the strong acid of the energetic anion desired. (Reaction 1).



Where H-X = HNO₃, HClO₄, or "H-N(NO₂)₂"

All of the product salts have relatively high melting points and were recovered in essentially quantitative yield. The nitrate salt melted at 205°C, the perchlorate salt at 196°C, and the dinitramide salt melted at 145°C. The DSC onsets were impressive for energetic salts, the nitrate had an onset of 250°C; the perchlorate did not begin to decompose until over 300° C; and the dinitramide salt didn't begin decomposing until 150° C. The impact and friction sensitivity values of all of these new salts were acceptable, as all were less sensitive than HMX, and in thermal stability studies carried out at 75° C, all of the materials had less than 1%/ day of mass loss.

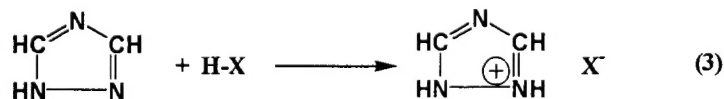
The synthesis of 4-amino-1, 2, 4-triazole is well known in the literature, and is the simple reaction between formic acid and hydrazine at elevated temperatures in presence of acid catalysts.³ The white crystalline solid of 4-amino-1, 2, 4-triazole has a melting point of 87° C, and is highly soluble in most polar organic solvents. Energetic salts of 4-amino-1, 2, 4-triazole were made in high yield through the simple reaction of one equivalent of 4-amino-1, 2, 4-triazole and one equivalent of the strong acid of the energetic anion desired. (Reaction 2).



Where H-X = HNO₃, HClO₄, or "H-N(NO₂)₂"

Since the starting material 4-amino-1, 2, 4-triazole, has a relatively low melting point of 87°C, it was hoped that the resultant salts would also have low melting points. In fact, all of the resultant salts have lower melting points than that of the starting heterocycle. The nitrate salt melted at 68°C, with a DSC onset of 180° C, the perchlorate salt at 73°C, with a DSC onset of 210° C, and the dinitramide salt melted at around 20°C, and had a DSC onset of 145° C. Both the nitrate and perchlorate salts of 4-amino-1, 2, 4-triazole were white crystalline solids, which were easily recrystallized. The dinitramide salt could not be made crystalline. However DSC studies of the dinitramide salt, revealed an endotherm indicative of a melt, at +20°C. Safety tests carried out on these salts found that the nitrate was relatively insensitive, but the perchlorate and the dinitramide were significantly more sensitive than HMX. All of the salts pass the thermal stability test at 75°C, losing less than 1% of their mass per day.

1, 2, 4-triazole has a melting point of 121°C, and it was found that the product salts all had relatively high melting points. The synthesis of the salts is identical to that of the 4-amino-1, 2, 4-triazole family, and 1, 2, 4-triazole, was very soluble in methanol, and all reactions were carried out in this media. (Reaction 3)



Where H-X = HNO₃, HClO₄, or "H-N(NO₂)₂"

1, 2, 4-triazole nitrate was a white crystalline solid with a melting point of 137°C, while the perchlorate salt was much lower at 89°C. The dinitramide salt was a white crystalline solid with a melting point of 75°C.

All of the materials had excellent safety properties, with all being less sensitive than HMX, and all, but the dinitramide salt passed the thermal analysis test at 75°C.

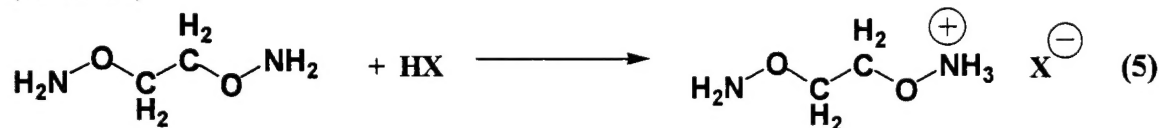
1, 2, 3-triazole is a liquid at ambient temperatures, and it was hoped that the salts might also have low melting points. The reaction scenario was the same as for the other salts and all reactions were carried out in methanol. (Reaction 4)



Where H-X = HNO₃, HClO₄, or "H-N(NO₂)₂"

The resultant salts of 1, 2, 3-triazole were low melting salts, but were solids at ambient temperatures. All of the salts were white crystalline materials, with the nitrate salt melted at 110°C, a DSC onset of 125°, the perchlorate salt melted at 73°C, with a DSC onset 220°C, and the dinitramide salt melted at 61°C, and had a DSC onset of 80° C. The safety tests were carried out on the nitrate and perchlorate salt, with the nitrate salt being relatively insensitive, but the perchlorate salt being very sensitive. On thermal analyses at 75° C, only the perchlorate salt had less than 1% per day mass loss.

Ethylene bisoxayamine, NH₂-O-CH₂-CH₂-O-NH₂, is a very energetic material which has been previously reported in the literature, both as the neutral⁴ and as its dihydrobromide salt.⁵ Since the methylene bisoxayamine has been significantly studied at AFRL previously⁶⁻⁸, we decided to investigate ethylene bisoxayamine to see if there were any marked difference between these two materials. The synthesis of monoprotonated salts of ethylene bisoxayamine, were easily made through the reaction of one equivalent of ethylene bisoxayamine with one equivalent of the strong acid of the desired energetic anion. (Reaction 5)



Where H-X = HNO₃, HClO₄, or "H-N(NO₂)₂"

The single salts of ethylene bisoxayamine were all crystalline solids, the nitrate salt melted at 76° C, DSC onset at 100° C; the perchlorate salt melted with decomposition at 137° C; and the dinitramide salt melted at 59° C and had a DSC onset at 75-80°C. The safety tests revealed sensitive materials with the perchlorate and dinitramide salts being extremely treacherous. All of the salts tested failed the thermal stability tests at 75° C. The double salts of ethylene bisoxayamine are made in similar fashion to Reaction 5 above, with the only difference being that two equivalents of strong acid are used to form the double salts. The dinitrate and diperchlorate salts of ethylenebisoxayamine were crystalline solids, but the bis(dinitramide) was a viscous oil which could not be crystallized. The dinitrate salt melted at 135°C, DSC onset at 165°C; diperchlorate salt melted at 123° C, DSC onset 185° C; and the bisdinitramide had a DSC onset at 120° C. The dinitrate had acceptable safety properties, but the diperchlorate and bisdinitramide salts were extremely treacherous materials.

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